



Current generation in membraneless single chamber microbial fuel cells (MFCs) treating urine



Carlo Santoro^{a,b,*}, Ioannis Ieropoulos^{c,d,**}, John Greenman^d, Pierangela Cristiani^e, Timothy Vadas^a, Allison Mackay^a, Baikun Li^{a,b,***}

^a Department of Civil and Environmental Engineering, University of Connecticut, 261 Glenbrook Rd, Unit 2037, Storrs, CT 06269-2037, USA

^b Center for Clean Energy Engineering, University of Connecticut, 44 Weaver Rd., Storrs, CT 06269-5233, USA

^c Bristol Robotics Laboratory, University of the West of England and University of Bristol, UK

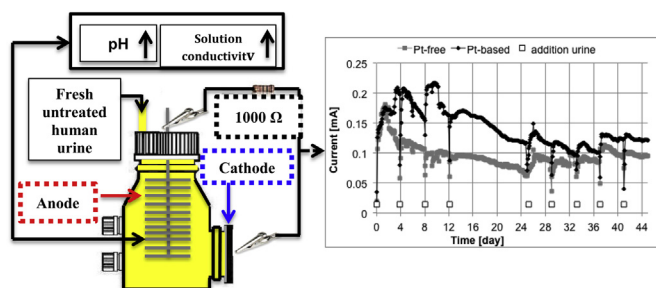
^d Faculty of Applied Sciences, University of the West of England, Bristol, UK

^e RSE-Ricerca sul Sistema Energetico S.p.A., Environment and Sustainable Development, Via Rubattino 54, 20100 Milan, Italy

HIGHLIGHTS

- Membraneless SCMFCs were used for treating human untreated urine.
- pH increased to 9.2 in SCMFCs due to urea hydrolysis.
- Anodic and cathodic kinetics were characterized over time.
- High pH had negative impacts on anodic performance.
- Pt-based cathode and Pt-free cathode had similar performance.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated a novel treatment process for human urine in membraneless single-chamber microbial fuel cells (SCMFCs). The performances of SCMFCs with Pt-based or Pt-free cathode were tested for over 1000 hours of operation. The pH of the anodic solution increased from 5.4–6.4 to 9.0 due to the urea hydrolysis, which consequently decreased the anodic performance even though the cathode was not affected, indicating that the MFCs were anode-limited. The solution conductivity increased up to 3 times the initial value. The initial current generated by the Pt-free cathodes SCMFCs was 0.13–0.15 mA, and stabilized at 0.1 mA. The Pt-based cathode SCMFC decreased from 0.18–0.23 mA to 0.13 mA. This study showed that high pH caused by urea hydrolysis lowered the anodic reactions and the SCMFCs overall performance. The Pt-free cathode performance was comparable to that of Pt-based cathodes, thus offering a cost effective alternative for future developments.

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* Corresponding author. Department of Civil and Environmental Engineering, University of Connecticut, 261 Glenbrook Rd, Unit 2037, Storrs, CT 06269-2037, USA. Tel.: +1 8604506782.

** Corresponding author. Bristol Robotics Laboratory, University of the West of England and University of Bristol, UK. Tel.: +44 0 1173286318x86322.

*** Corresponding author. Department of Civil and Environmental Engineering, University of Connecticut, 261 Glenbrook Rd, Unit 2037, Storrs, CT 06269-2037, USA. Tel.: +1 8604862339.

E-mail addresses: carlo.santoro@uconn.edu, ka.santo@hotmail.it (C. Santoro), ioannis.ieropoulos@brl.ac.uk (I. Ieropoulos), baikun@uconn.edu (B. Li).

1. Introduction

Microbial fuel cells (MFC) are a promising bio-technology for utilizing organic compounds to generate electricity. Several organic wastes (e.g. municipal wastewater [1,2]), food processing wastewater [3], meat processing wastewater [4], starch [5], landfill leachate [6] and others [7]) have been tested in MFC systems in terms of organic removal and electricity production. Recently, human urine has been identified as a suitable fuel for MFCs [8], since it contains high amounts of organic compounds, nitrogen, phosphorous and sulfate [9]. Traditional 2-chamber MFCs fed with human urine have been successfully operated for 2 years [8] and recently mini-stacked MFCs were tested with the same substrate [10].

The cost-effective removal of nitrogen and phosphorous in wastewater treatment is critical to solve eutrophication in natural water resources. Human urine accounts for 75% of the nitrogen and 50% of the phosphorous content in municipal wastewater [9] and as such, the removal of nitrogen from human urine could reduce the nutrient discharge in wastewater. Traditional MFCs with a membrane electrode assembly (MEA) fed with human urine (after centrifugation pretreatment) was examined [11] and ammonia was recovered through volatilization and absorption. Meanwhile, other studies [12] recovered phosphorous from human urine using struvite precipitation before feeding into MFCs.

Until now, no study has utilized membraneless single chamber MFCs (SCMFCs) with air-cathodes for human urine treatment in long-term operation (e.g. over 1000 h). Even though the removal of nutrients (nitrogen and phosphorous) and organic contaminants (chemical oxygen demand, COD) were studied in MFCs treating urine, the fundamental electrochemical mechanisms have not been clearly understood. Therefore, the main goal of this paper was to investigate the anode and cathode electrochemical characteristics for long-term operation of MFCs treating urine. In addition, most MFC studied used costly platinum (Pt) as cathode catalysts [2]. In

order to reduce the MFC costs, novel low-cost electrodes should be developed. Pt-free cathodes were developed as the substitute for Pt in single chamber MFCs fed with municipal wastewaters [13,14]. But there has been no effort to utilize Pt-free cathode in MFCs to treat urine.

This study aimed at addressing these questions. Firstly, the dynamics of the pH and solution conductivity in batch-mode SCMFCs treating human urine were measured and analyzed over 1000-hr operational periods. The feeding cycles of human urine ranged from 1 day to 4 days to investigate the SCMFC performance at different organic loading rates. Secondly, the effects of pH and solution conductivity on anode and cathode process over the operational periods were determined through electrochemical tests (Linear Sweep Voltammetry, LSV). Finally, the performance of Pt-based cathodes and Pt-free cathode was compared to explore the potential of low-cost electrode materials for real world implementation. Throughout the experiments, human urine was directly fed into SCMFCs without any pretreatment in order to reduce operational cost.

2. Materials

2.1. SCMFC setup and electrode materials

Batch-mode membraneless SCMFCs with 130 mL anode chambers and air-cathodes were used in this study and were set-up as previously described [13] (Fig. 1). Carbon brush (size 6×4 cm as projected area, Mill-Rose Carbon Fiber Brush Anode) was the material used for the anode electrodes. Carbon cloth (30wt PTFE, E-Tek) was used as cathode support (Fig. 1b), and coated with a micro porous layer (MPL) conductive ink [14] (Fig. 1c and d) using a silk screen technique. The MPL layer was capable of enhancing oxygen transfer inside cathode structures and also increase the electrical conductivity of cathodes [13].

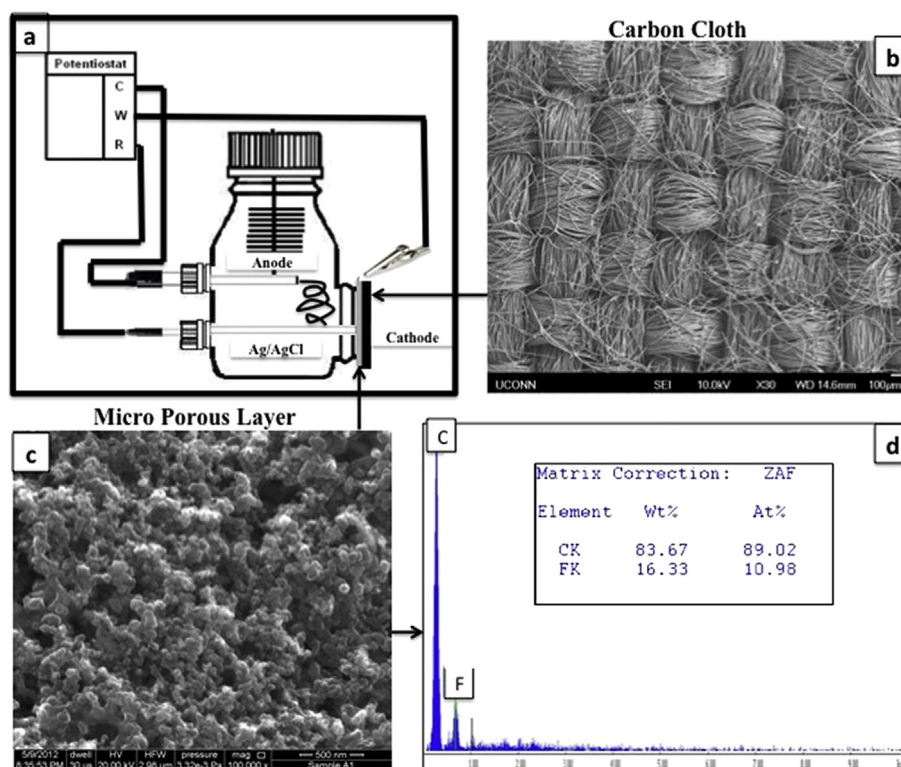


Fig. 1. The LSV measurement of cathodes in SCMFCs. (a) Three electrodes configuration for cathode LSV in SCMFCs, (b) the SEM image of the carbon cloth (as cathode support), (c) the SEM image of the MPL on cathode, and (d) the EDX results of the MPL.

In the Pt-free cathode configuration, the MPL was facing directly the anodic solution. In the Pt-based cathode configuration, a layer of catalyst with loading $0.25 \text{ mgPt cm}^{-2}$, was applied on the MPL [15] and then placed facing the anodic solution. The cathode geometric area was 5 cm^2 in all SCMFCs tested. The cathode electrodes were sealed on the lower part of the SCMFCs. The outer side of the MPL (gas diffusion layer, GDL) cathode was exposed to air.

2.2. Feeding cycles of human urine

The substrate for the SCMFCs was human urine from a healthy individual without any pretreatment. Prior to the SCMFC tests, the anode (carbon brush) was inoculated with raw wastewater (wastewater treatment plant, University of Connecticut) and sodium acetate solution (concentration: 3 g L^{-1}) for 4 weeks.

Human urine was fed into the anode at three duration times (1 day, 2 days, and 4 days) to examine the MFC performance at different substrate loadings. All SCMFCs were operated continuously for over 1000 h (42 days). It should be noted that the SCMFCs were operated from Day 12 to Day 25 without replacing the urine solution. All experiments were operated at ambient temperature $30 \pm 2^\circ \text{C}$.

3. Methods

3.1. Solution conductivity, pH and chemical oxygen demand (COD) measurements

Electrical solution conductivity and pH in the anode chamber of SCMFCs were measured daily using a portable conductivity meter (Orion 3 Star, Thermo Scientific) and a portable pH meter (Thermo Fisher Scientific Orion 3-star). The chemical oxygen demand (COD, g L^{-1}) of the solution was measured using HACH high range ($0\text{--}15 \text{ g L}^{-1}$) COD vials and DR 220 spectrophotometer (HACH, Loveland, CO) following the standard procedure.

3.2. SCMFC current generation

An external resistance (R_{ext}) of 1000Ω was used for all tested SCMFCs. The voltage (V) across this R_{ext} was recorded every 2 h using a Keithley 2700 data logging system. Based on the R_{ext} and the V , the current (I) were calculated according to Ohm's law ($I = V/R$).

3.3. Electrochemical measurements of SCMFCs

Electrochemical analysis of anodes and cathodes in SCMFCs was performed using linear sweep voltammetry (LSV) in a three-electrode configuration (Fig. 1a), with platinum wire as the counter, Ag/AgCl ($+197 \text{ mV}$ vs standard hydrogen electrode, SHE) as the reference, and anode or cathode (subject) as the working electrodes. A potentiostat (Gamry P600) was used to perform the LSV tests at a low scan rate [16]. The anode scan rate was 0.1 mV s^{-1} and the cathode scan rate was 0.2 mV s^{-1} . The voltages are expressed vs the SHE. The scanning electron microscope (SEM) images showed the external cathode support (Carbon cloth 30%wt Polytetrafluoroethylene (PTFE) treated) (Fig. 1b) and the MPL of the cathode (Fig. 1c) used in this study. EDX (Energy-dispersive X-ray spectroscopy) spectral analysis verified the absence of Pt on the Pt-free MPL cathodes and the presence of fluorine on the PTFE utilized as a ligand for the MPL (Fig. 1d).

4. Results

4.1. The trend of solution conductivity and pH over time

The daily values of solution conductivity (SC) in fresh human urine varied from 7 to 20 mS cm^{-1} , due to the natural fluctuation of

the salt contents in human urine (Fig. 2a). After Day 1, the SC increased to approximately 3 times compared to the initial values ($21\text{--}63 \text{ mS cm}^{-1}$), probably due to the breakdown of urine compounds and consequent release of ions (e.g. ammonium ions) from urea hydrolysis into the solution [17,18]. The SC value eventually reached a plateau from Day 2 to Day 4 (for the 4-day cycle). The trend of the Pt-based and Pt-free cathode SCMFCs was identical (Fig. 2a) and the increase in conductivity was expected to reduce the ohmic resistance of the liquid electrolyte even if it was found that the increase in solution conductivity did not affect the anode or cathode performance [19].

The daily values of pH in fresh human urine varied between 5.4 and 6.4 (Fig. 2b), which was in agreement with previous studies [20]. The pH rapidly increased to 9 ± 0.2 after Day 1, possibly due to urea hydrolysis and ammonium ions formation [21,22], which can be accelerated at elevated temperatures (30°C) [18]. The pH then stabilized at 9 ± 0.2 between Day 2 and Day 4 (for the 4-day cycle) (Fig. 2b).

Daily ammonium ions concentration was not specifically shown in this work. The concentration varied from 0.3 to $1.1 \text{ gNH}_4^+\text{-N L}^{-1}$ initially (fresh urine) to up to $3.9\text{--}4.3 \text{ gNH}_4^+\text{-N L}^{-1}$ (after Day 1) [23]. This rapid rise confirmed the urea hydrolysis in the anodic chamber and the concentration was comparable with other studies [17,18,20–22]. The highest concentration ($4.5\text{--}4.7 \text{ gNH}_4^+\text{-N L}^{-1}$) reached in the later days [23]. Those data proved the cause of the increase in pH and solution conductivity. Phosphorous concentration was also measured and the $20\text{--}50\%$ removal efficiency was

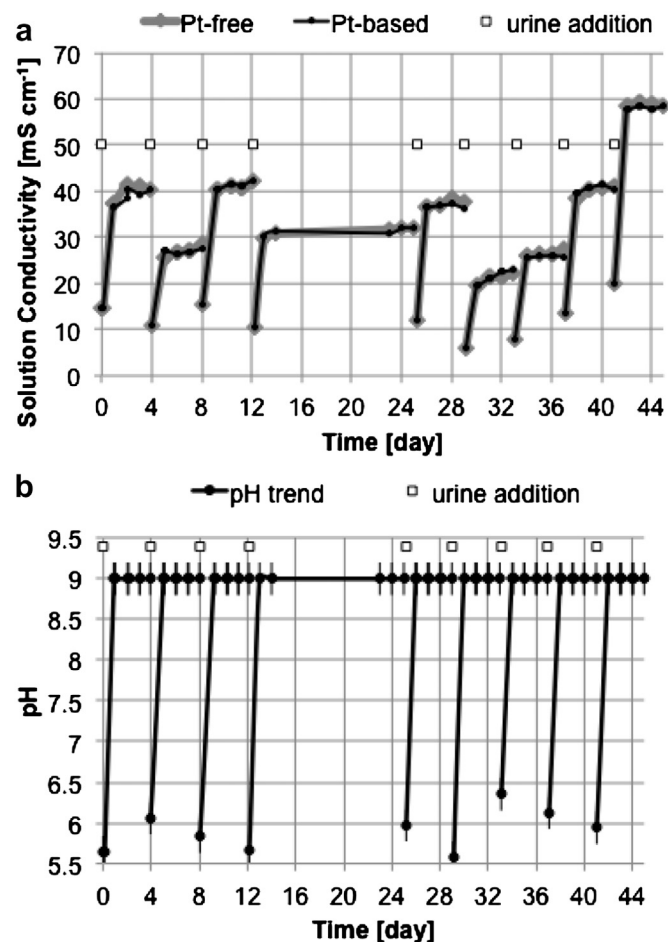


Fig. 2. Variation of urine conductivity (a) and pH (b) over the 4-day cycles during the experimental period.

observed in a 4-day cycle [23]. The phosphorus removal was mainly attributed by the compounds precipitation at high pH [18].

4.2. Current generation of SCMFCs at different urine feeding cycles

The SCMFCs with Pt-based cathodes had better performance than those with Pt-free cathodes, but this difference decreased over time (Fig. 3). The difference between Pt-based and Pt-free cathodes was approximately 50–100% in the start-up stage, and reduced to 20–30% at the end of tests. The lower performance of Pt-based cathodes over time was probably caused by the deactivation of Pt from the sulfur contained in urine [24] and the precipitation of compounds on the cathode surface at high pH (Fig. 2a) [18]. In contrast with the rapid decrease in current generation from the Pt-based cathodes, the Pt-free cathodes exhibited a relatively stable performance (Fig. 3). These findings indicated that Pt-free cathodes

could offer a good low-cost alternative for Pt-based cathodes in terms of current generation of MFCs treating urine.

The current generation of SCMFCs was determined at different urine feeding cycles (1, 2 and 4 days) for over 1000 h (Fig. 3). The urine feeding cycles only caused slight differences in current generation, especially in the SCMFCs with Pt-based cathode (Fig. 3). For Pt-based cathode MFCs, the current generation of 1-day cycle was slightly higher than 2-day or 4-day cycles from Day 0 to Day 8. But from Day 8 to Day 16, 1-day cycle became lower (20–30%) than the 2-day or 4-day cycles. After Day 16, the current generation of 1-, 2- or 4-day cycle was close (difference within 5–10%). This could be caused by high pH (9 after Day 1, Fig. 1) that enhanced the precipitation of the compounds on the cathode, and reduced the difference from the feeding cycles over time. The complete refresh of the urine solution in the 1-day cycle SCMFCs was more frequent than 2-day or 4-day cycles, so that the precipitation of compounds was accelerated and more deposits was present on the cathode surface, consequently the Pt catalyst was covered and poisoned after a short period.

For the Pt-free cathode SCMFCs, the feeding cycles did not cause significant difference in current generation, except between day 14 and day 20 when the 1-day cycle has higher current generation (20–30%) than 2-day and 4-day cycles. At the start-up stage, the current generation decreased (due to high pH) and then gradually increased over time (Day 4, Day 12; Fig. 3), followed by a substantial decrease between Day 12 to Day 25 (solution not being replaced during this period), and finally reached a plateau. All the SCMFCs demonstrated the similar trends of current production at three feeding cycles, with a difference of less than 10% after the plateau was reached (Day 25). The initial current generation of the Pt-free cathode SCMFCs ranged at 0.13–0.15 mA, and then stabilized at 0.09–0.11 mA. The initial current generation of the Pt-based cathode SCMFCs ranged 0.18–0.23 mA, then decreased to 0.11–0.14 mA.

It should be noted that in some cases, a slight decrease in current generation was observed immediately after the addition of urine, which was partially caused by the oxygen (present in the feeding solution) stress on the anodophilic bacteria of the anodic biofilms, and by the pH stress (3 log-folds in terms of H^+ ion concentration). The peak current production was generally achieved on Days 1 and 2 after the addition of urine. The subsequent decrease in current production was probably due to the decay resulting from batch mode operation. The loss in current production of Pt-based SCMFCs was between 50 and 100% over 1000 h of operations, while the loss in the Pt-free cathode SCMFCs was only 25–50%.

4.3. Anode and cathode electrochemical performance

The degradation and hydrolysis of urine caused the changes of the solution conductivity, pH, and substrate concentration, which then affected the performance of the anodes and cathodes. Electrochemical characteristics of individual electrodes (anode or cathode) were determined by the LSV measurements using the three-electrode technique.

The anodic LSV exhibited a significant decrease over time. Particularly, the best anodic performance with currents higher than 2.5 mA (-0.17 V vs SHE) was achieved before the addition of human urine into the SCMFCs (Day 0, Fig. 4a). After the addition of urine, the anode performance decreased significantly over time (Day 5 and Day 38, Fig. 4a). The COD concentration of the anodic solution was higher than 7 g L^{-1} , which meant there was always sufficient organic substrate for anodic biofilms in SCMFCs. It had previously been found that an increase in ammonia concentration (up to $4 \text{ g NH}_4\text{-N L}^{-1}$) and salinity (conductivity) in the anode did not affect the MFC performance [17], which might be related to the neutral

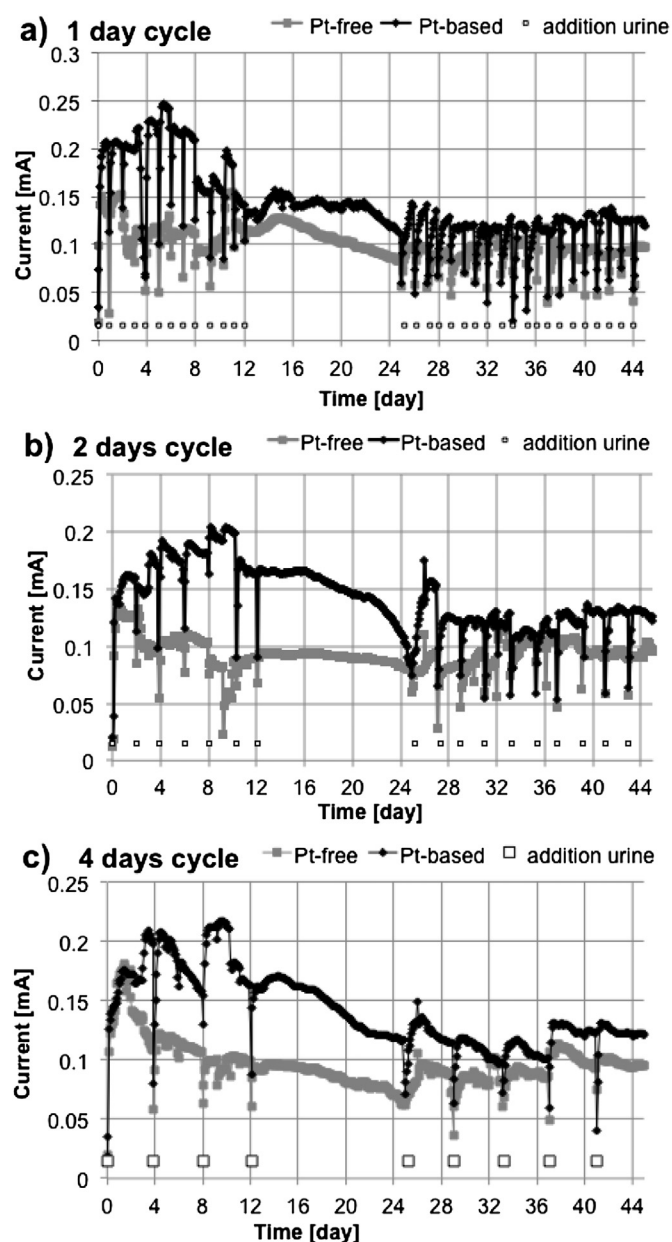


Fig. 3. The current generation of SCMFCs with Pt-based cathodes and Pt-free cathodes at different urine feeding cycles (a: 1-day, b: 2-day, c: 4-day).

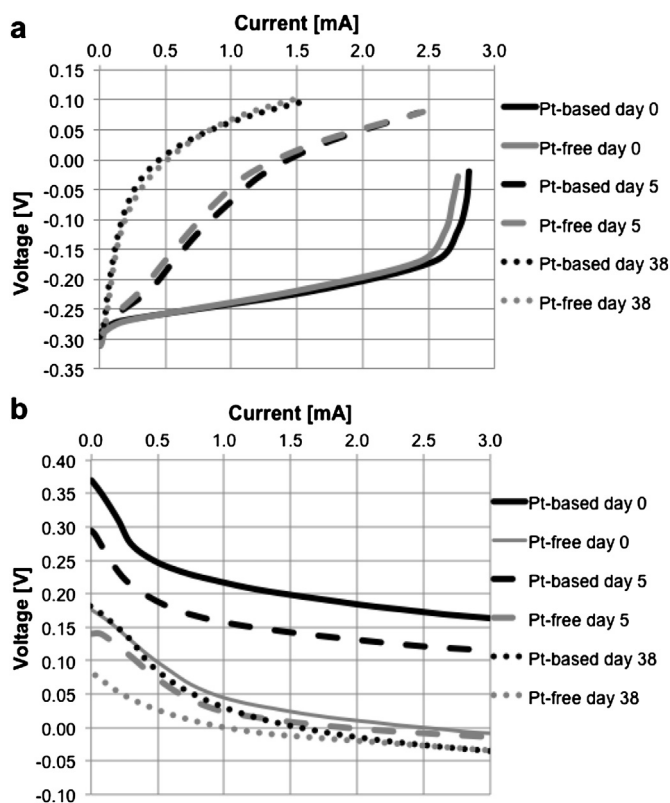


Fig. 4. Variation of Anodic LSV (a) and Cathodic LSV (b) over the experimental period. Day 0 (before the urine feeding, Solution conductivity (SC): $4.7 \pm 0.1 \text{ mS cm}^{-1}$, COD: $2.8 \pm 0.1 \text{ g L}^{-1}$, pH 7.6 ± 0.2), Day 5 (SC = $26.3 \pm 0.7 \text{ mS cm}^{-1}$, COD: $7.0 \pm 1 \text{ g L}^{-1}$, pH = 9.0 ± 0.2) and Day 38 (SC: $39.1 \pm 0.5 \text{ mS cm}^{-1}$, COD: $7.5 \pm 0.5 \text{ g L}^{-1}$, pH 9.0 ± 0.2).

pH recorded in that study. In fact, the anodic LSV curves before the addition of urine (Fig. 4a) are similar to the reported values [17]. A possible reason for the deterioration of the anodic LSV curves (Fig. 4a) was the significant change in pH throughout the urine degradation (from 5.4 to 6.4 to 9.0 ± 0.2 , Fig. 2b).

The negative impact of high pH on the anode performance of MFCs was found in previous studies [25,26]. Neutral pH (7–8) was optimal for the anodic reactions and bacterial activity, and the anodic polarization resistance was half at neutral pH compared with those at other pH values (<7 and >8) [25]. In this study, pH rapidly increased from acidic (pH 5.4–6.4) to alkaline (around 9.0) levels due to the urea hydrolysis, which stressed the anodic microbial communities and lowered the performance [26]. Consequently, anodic kinetics became slower over time (especially for low potential values (from -0.3 to -0.05 V) at Day 5 and Day 38, Fig. 4a) and the power generation was severely reduced (Fig. 3).

With respect to the cathode performance, it was previously reported that an increase in the anodic pH (from 5 to 9) of a SCMFC substantially lowered the cathodic polarization resistance and enhanced the reaction rates [25]. Other studies showed a significant increase in the oxygen reduction reaction (ORR) kinetics in an alkaline electrolyte [27,28], even though the redox potential of the ORR was significantly lowered at high pH [29]. However, a decreasing trend was observed on the cathodes at high pH levels in this study. In particular a significant decrease in open circuit potential (OCP, the initial point on each LSV curve) was observed in all the SCMFCs tested (Fig. 4b). The OCP values and LSV curves of the Pt-based cathodes were always higher than those of the Pt-free cathodes, due to the better catalytic activity of Pt. However the advantage of Pt as a catalyst diminished significantly over time, which might be the result of salt precipitation on the cathode surface of the Pt layer or the progressive poisoning of Pt over time by the contaminants in urine. It is possible that salt precipitation blocked the cathode pores and reduced oxygen diffusion. The cathode images taken over the 45-day operational period proved this hypothesis, and showed the precipitant on the cathode (Fig. 5a). After 8 days, a clear white deposit was observed on the cathode of the SCMFCs. A much thicker deposit was detected at the end of the operations after 45 days (the cathodes were dried). The SEM/EDX images identified the precipitation as mainly carbon–calcium–magnesium–phosphorous based compounds (Fig. 5b). Those compounds were found previously as carbonate species and phosphate species (struvite, k-struvite and hydroxyapatite) [18,23]. Moreover, a light peak of sulfur was identified in the spectrograms

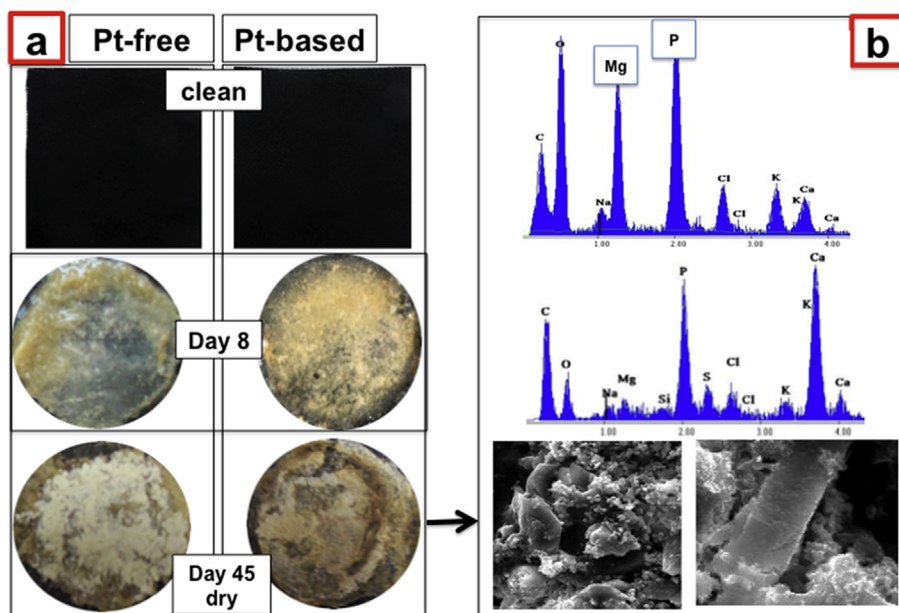


Fig. 5. The top view of the cathodes (a) (fresh cathodes, cathodes after 8 days of operation, and cathodes after 45 days of operation) and the SEM/EDX images of the deposition on cathodes (b).

(Fig. 5b). It was reported previously that sulfur deactivated significantly the catalytic activity of Pt [24]. This could be another reason for the steady decrease in current generation of the Pt-based cathode SCMFCs.

The cathode LSVs confirmed the decrease in current generation over time for batch mode SCMFC systems (Fig. 4). The slight disadvantage of Pt-free cathodes over Pt-based cathodes (initially over 50% and then 20–30% lower than Pt-based cathodes over time) might be compensated by the low cost of the MPL alternative. For the range of currents investigated (up to 2 mA) (Fig. 4a), the most significant limiting factor in the MFC performance was the anode behavior. Nevertheless, these results demonstrated that the current production of SCMFCs treating human urine is significantly affected by the pH, the anaerobic bacterial activity, and cathodic reaction rates. It should be noted that the decrease in the cathode OCP values found in this study was faster than previously reported for the same cathode materials with a different anolyte (domestic wastewater and sodium acetate) [14].

4.3.1. The LSVs of anodes and cathodes in a 4-day cycle

Along with the anodic/cathodic LSV curves over the 1000-hr operational period, the anodic/cathodic LSV curves in a 4-day cycle was also measured to elucidate the daily variation of the electrode performance with pH, solution conductivity, and COD concentration in a batch-mode operational cycle (Fig. 6). The initial LSV (Day 0, that was Day 37 in the SCMFC operational period) was

performed after the addition of urine into the solution. The anodic OCP (the initial point of the LSV) at Day 0 was -0.25 V (vs SHE), probably due to the introduction of oxygen during the addition of urine and the redox-stress resulting from the increase in H^+ ion concentration. The OCP then dropped to $-0.3/-0.34$ V (vs SHE) on Day 1 (that was Day 38 in the MFC operational period) and stabilized at these values (Fig. 6a), indicating the reinstatement of anaerobic conditions inside SCMFCs.

The anodic LSV curves (Fig. 6a) correlated well with the current generation (Fig. 3). The best anodic kinetics were achieved on Day 1, which was 1 day after the addition of urine. A slight decrease occurred in the following days (Day 4, that was Day 40 in the MFC operational period) (Fig. 6a). The initial COD concentration 10.9 g L^{-1} decreased to 7.5 ± 0.5 g L^{-1} on Day 1, and 3.6 ± 0.3 g L^{-1} on Day 4. Since the final COD concentration in a 4-day cycle was still high (approx. 3.6 g L^{-1}), it was not the limiting factor for anodic performance.

The introduction of oxygen in the solution on Day 0 was also confirmed in the cathodic LSV curves, which showed the cathodic OCP (the initial point on LSV curve) being slightly higher than the ones in Day 1 and Day 4 (Fig. 6b). The increase in solution conductivity (tripled after Day 1, Fig. 2a) and the increase in pH from slightly acidic (<7) to alkaline (up to 9.2) conditions, enhanced the ORR reactions on the cathodes (Fig. 6b). Even though the COD concentration of the solution did not affect the cathodic performance, it was previously found that the increase in the ionic strength of the electrolyte (from 7.5 mS cm^{-1} to up 31.3 mS cm^{-1}) did not affect power generation and cathodic performance [19]. Moreover, the high pH of the electrolyte enhanced the ORR rate on the cathodes, as previously reported [25,27,28].

The advantage of the Pt-based cathode over Pt-free cathodes was visible at current levels lower than 1.5 mA, but then the Pt-based and Pt-free cathodes exhibited the same behavior at higher currents. These LSV curves confirmed the better performance of the SCMFCs with Pt-based cathode compared to the ones with Pt-free cathode (Day 37 to Day 40, Fig. 3c).

The membraneless SCMFCs were used to utilize the organic compounds in human urine and transform them into electricity during the operational period of over 1000 h. An initial drop in current production was noticed, but then followed by a stable production, probably due to the adaptation of anaerobic bacteria to high pH (>9.0) and high ammonia concentration (up to 5 g NH_4-N L^{-1}). This study showed that high pH limited significantly the anode performances and damaged the anodic mesophilic communities. Consequently the overall MFCs performances were compromised to some extents. It should be addressed that the batch-mode SCMFC systems used in this study were not optimized for high power generation of urine treatment. Continuous flow MFC processes, more efficient mixing devices, and the improved MFC configurations should be developed to lower the high pH and organics gradients in MFC systems. The addition of a natural buffering solution or a natural acidic waste could be a solution to lower the pH in MFCs.

This long-term MFC study clearly demonstrated that human urine can be effectively degraded in SCMFCs with stable current generation, even though the current generation was relatively low. High amounts of human urine generated globally and high concentrations of organic compounds in human urine make it a potential fuel for power production in MFCs to power electronic devices [30] and robots [31,32]. Moreover, utilizing human urine in MFCs is a good example of natural waste products being directly converted into electricity without any pretreatment, which is self-sustainable waste treatment process. The use of Pt-free could significantly reduce the capital costs of MFCs, which illustrates the great potential for real-world application.

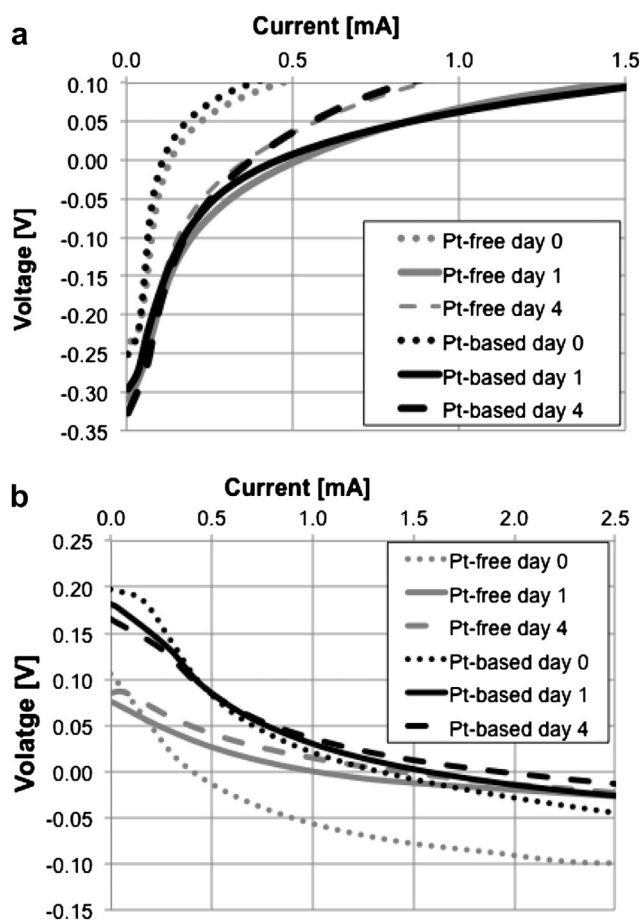


Fig. 6. The daily variation of anodic LSV (a) and cathodic LSV (b) in a 4-day cycle. Day 0 (SC: 13.5 mS cm^{-1} , COD: 10.9 g L^{-1} , pH 6.2), Day 1 (SC: 39.1 ± 0.5 mS cm^{-1} , COD: 7.5 ± 0.5 g L^{-1} , pH 9 ± 0.2) and Day 4 (SC: 40.8 ± 0.4 mS cm^{-1} , COD: 3.6 ± 0.3 g L^{-1} , pH 9 ± 0.2) in a 4 days cycle.

5. Conclusions

This study was the first to extensively investigate the performances of human urine using membraneless SCMFCs with Pt-based and Pt-free cathodes. It was found that both pH and conductivity rapidly increased after the addition of human urine due to the urea hydrolysis in the anode chamber. High pH had a negative effect on the anodic process over time and limited the overall MFC performance. In contrast, high pH enhanced the ORR kinetic on cathodes, even though the salt deposition on the surface appeared to be accelerated. Finally, the advantages of Pt-based cathodes over Pt-free cathodes reduced over time.

Acknowledgments

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